

CORROSION OF BIOCOMPATIBLE $Mg_{66+x}Zn_{30-x}Ca_4$ ($x=0.2$) BULK METALLIC GLASSES

The aim of this paper was to investigate the corrosion resistance of $Mg_{66}Zn_{30}Ca_4$ and $Mg_{68}Zn_{28}Ca_4$ metallic glasses and evaluate the ability of this amorphous alloy use for medical applications as biodegradable medical implants. Taking into account the amount of Mg, Zn, Ca elements dissolved in multielectrolyte physiological fluid (MPF) from $Mg_{66+x}Zn_{30-x}Ca_4$ ($x=0.2$) alloys the daily dose of evolved ions from alloys components was determined. Additional goal of the paper was determination of corrosion rate (V_{corr}) and amount of hydrogen evolved from amorphous magnesium alloys in simulated environment of human body fluids during 24h immersion and during electrochemical tests. Corrosion studies were done in the multielectrolyte physiological fluid (MPF) at 37°C. The amount of hydrogen evolved [ml/cm^2] and corrosion rate V_{corr} [$mm/year$] of amorphous $Mg_{66}Zn_{30}Ca_4$ and $Mg_{68}Zn_{28}Ca_4$ alloys were compared. The work also presents characterization of Mg-based bulk metallic glasses structure in the form of 2 mm thickness plates. Samples structure was analyzed by means of X-ray diffraction. Fracture and surface morphology of magnesium alloy samples were identified using scanning electron microscopy.

Keywords: Mg-based alloys; bulk metallic glasses; amorphous structure; corrosion properties; biodegradable metallic alloys; corrosion products

1. Introduction

Until now the most commonly used materials for implants are titanium alloys. Chemical composition of implant determines nature of its changes in the living organism. Metal alloys for the biomaterials should also have good corrosion resistance towards tissues and body fluids environment and mechanical properties, which are required for load transfers. Metals in the specified concentration present in the implant composition, such as nickel, chromium, cobalt and molybdenum, can cause allergies manifested as lesions [1]. Many researchers modify the titanium implant surface to provide long-term protection of the patient body against toxic components [2]. An increasing interest of using corrodible metals in a huge number of medical applications is observed nowadays. A new class of biodegradable metallic alloys as the implants corrode gradually in vivo, without toxic response to patients elicited by released corrosion products. After that, they dissolve completely from bone to assist with tissue healing with no implant residues [3]. Therefore, the best alloying elements for the implants are these, which are present in the human body in high concentrations. These materials could be assumed as macroelements or microelements of special importance to human health, so their possible additional dose will not cause adverse health effects. Magnesium, as one of the main macroelements required for the proper functioning of the human organism is taken into account as biodegradable material for the implants. In fact, pure magnesium has low corrosion

resistance and not sufficient enough mechanical properties, which in turn disqualifies magnesium as material for medical implant. Initially, in the context of the biodegradable implants some investigations were carried out on industrial magnesium alloys, for example: AZ31, AZ91, WE43, LAE442 [4]. Unfortunately, magnesium alloys which contained aluminum (AZ31) and heavy metals were excluded. These additives are toxic and harmful to human body. The study of biodegradable alloys was limited, except alloys which contain biocompatible elements and/or small amounts of rare earth elements, which are tolerated by human body in suitable concentrations. Over the last decade new kinds of degradable Mg-based alloys for medical implants were reported: Mg-Ca [5], Mg-Zn [6], Mg-Zn-Ca (-Mn, -Si) [7], Mg-Y [8], Mg-Y-Zn [9], etc.

Dissolution rate of magnesium alloys under certain conditions defined by the human body fluids depends on their structure and chemical composition. Single-phase structure of amorphous alloys is related to the high corrosion resistance. These properties may cause more uniform progress of implant corrosion [10]. In this work, metallic glasses based on magnesium with zinc and calcium addition were tested as the potential metallic biomaterials for biodegradable medical implants.

2. Material and methods

The studies focused on the $Mg_{66}Zn_{30}Ca_4$ and $Mg_{68}Zn_{28}Ca_4$ (at.%) bulk metallic glasses in the form of plates with 2 mm

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diameter. Due to significant difference in melting temperatures of Mg, Zn and Ca, main formation process of alloys consisted of two steps. In the first step Mg and Zn were melted using the Techma-Elcal Rel-15 induction generator. Then, calcium was added to the binary Mg-Zn alloy. In inert atmosphere master alloys were re-melted using an induction melting and then injected into water cooled copper mold by the pressure casting method [11-13].

Research on the sample structures was carried out using the PANalytical's X'Pert Pro X-ray diffractometer with $\text{Co}_{\text{K}\alpha}$ radiation. Measurement was done in the range from 30° to 90° of 2θ angle. The fracture morphology of glassy samples in the form of rods in as-cast state was analyzed using Supra 35 Carl Zeiss scanning electron microscope.

To determine the amount of hydrogen evolution from the Mg alloys immersion tests in multi electrolyte physiological fluid (MPF) were done. Since the studied alloys are destined to serve as a biomaterial, the MPF solution was chosen to the tests. Chemical composition of the MPF fluid is similar to the human blood composition (Table 1). The corrosion tests were carried out in multielectrolyte physiological fluid at 37°C . Before the corrosion tests the samples were polished and purified ultrasonically in acetone. Immersion time for each fluid was 24 hours. Magnesium alloys during dissolution process (corrosion process) in simulated body fluid evolve hydrogen. Its volume was measured using gas burette. One ml of the released H_2 is stoichiometrically equivalent to 1 mg of magnesium dissolved, and therefore the measurement of hydrogen evolution corresponds to indirect measurement of biodegradability and corrosion effects within the magnesium alloy. Evolved hydrogen is derived mainly from the local corroding area, what means, that the rate of hydrogen evolution is able to reliably reflect the local degradation rate of magnesium alloys [14,15].

Corrosion resistance of the alloys was also investigated using potentiodynamic polarization method. Measurements were performed with a scan rate of 1 mV/s, at a temperature 37°C in the MPF solution with free access to air. The surface state of the samples was stabilized at open circuit during 5 hours, immediately before the potentiodynamic measurement within the -150 mV vs. E_{OC} to $+150$ mV vs. E_{OC} range. An AutoLab PGSTAT100N potentiostat/galvanostat (Metrohm) and typical electrochemical cell with a three-electrode configuration with a saturated calomel electrode (SCE) as the reference electrode and platinum gauge as a counter electrode were used in the electrochemical measurements. Based on the obtained results, the corrosion potential (E_{corr} , V), corrosion current density (j_{corr} , A/cm 2) and polarization resistance (R_p , $\Omega\cdot\text{m}^2$) were determined.

To determine the detailed amounts of dissolved Mg, Zn, and Ca after 24h immersion, the studies on chemical composition of MPF solutions (corrosion medium) were done. Content of calcium, magnesium and zinc in MPF solution before and after immersion tests was determined using inductively coupled plasma atomic emission spectrometry (ICP-AES) Varian 710-ES spectrometer equipped with V-groove nebulizer and reduced-volume Sturman-Masters type spray chamber made of poly(tetrafluorethylene). The following parameter values were used: RF power 1.0 kW, plasma flow 15 L/min, auxiliary flow 1.5 L/min, nebulizer pressure 210 kPa,

pump rate 15 rpm, emission lines of Ca: $\lambda=211.276$ nm, Mg: $\lambda=278.142$ and 202.582 nm, Zn: $\lambda=206.200$, 213.857 nm. Calibration curve method was used and the calibration curves were established using the matrix (MPF solution) of the same concentration as in the samples. Metals content in the matrix solutions was determined using standard addition method. Calcium, magnesium and zinc standard solutions of 1 mg/mL (Merck Millipore, Germany) were used. Deionized water was prepared using the Millipore Elix 10 system. The obtained results represent an average of concentrations resulting from all analytical lines used with standard deviation not exceeding 1%.

3. Results and discussion

The results of X-ray diffraction investigations revealed that the examined $\text{Mg}_{66}\text{Zn}_{30}\text{Ca}_4$ and $\text{Mg}_{68}\text{Zn}_{28}\text{Ca}_4$ samples, in the form of plates with 2 mm diameter, were amorphous (Fig.1). SEM images showed, that fractures of magnesium alloy plates studied show characteristic "shell" patterns for amorphous metallic alloys (Fig.1). Song et.al [14] described, that the "shell" patterns are characteristic for the brittle amorphous metallic alloys. The areas of "shell" forms are located at the sample edges and through direct liquid-metal contact where the walls of the copper mold were formed. It may be related to alloy shrinkage during its solidification and the casting stresses.

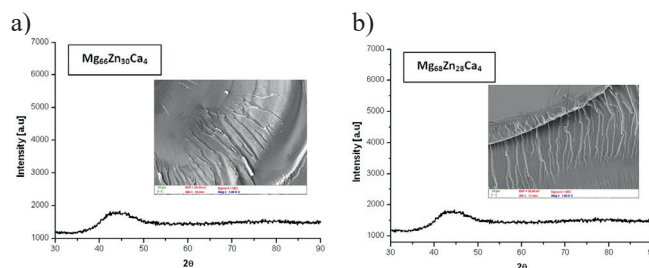


Fig. 1. X-ray diffraction pattern and SEM micrograph of the fracture morphology of a) $\text{Mg}_{66}\text{Zn}_{30}\text{Ca}_4$ and b) $\text{Mg}_{68}\text{Zn}_{28}\text{Ca}_4$ plates of 2 mm thickness

Electrochemical corrosion tests were carried out in MPF fluid at 37°C . During the OCP tests (Fig.2) growth of the measured potential was observed for both examined magnesium alloys, which may be related to selective digestion of the more active metals - components of the alloy (Mg, Ca). Progress of these processes for $\text{Mg}_{68}\text{Zn}_{28}\text{Ca}_4$ alloy is more variable than in the case of $\text{Mg}_{66}\text{Zn}_{30}\text{Ca}_4$. However, after cca. 4 hours (starting after initial 14000 s in OCP curves, Fig.2) in both amorphous alloys stabilization of the E_{OC} value is observed, which is $-1,2\text{V}$ for $\text{Mg}_{68}\text{Zn}_{28}\text{Ca}_4$ and $-1,18\text{V}$ for $\text{Mg}_{66}\text{Zn}_{30}\text{Ca}_4$. The OCP values for two Mg-Zn-Ca amorphous alloys are clearly higher than that of pure Mg sample. Amorphous $\text{Mg}_{66}\text{Zn}_{30}\text{Ca}_4$ alloy sample indicates more positive OCP value than that of amorphous $\text{Mg}_{68}\text{Zn}_{28}\text{Ca}_4$ alloy, possibly attributed to the different amount of Zn in the two Mg-Zn-Ca samples, since the electrode potential of Zn (-1.12V) is more positive than of Mg (-1.78V) [17]. The E_{OCP} value of pure Mg ($-1,78\text{V}$) corresponds to value from OCP curves presented by Wang et al. [18]. The results of potentiodynamic tests (Fig. 4,

Tab. 1) clearly show, that the $Mg_{66}Zn_{30}Ca_4$ and $Mg_{68}Zn_{28}Ca_4$ alloys demonstrate worse corrosion resistance than zinc and magnesium, which are alloying elements. The $Mg_{66}Zn_{30}Ca_4$ alloy exhibited similar electrochemical characteristics (current density $93 \mu A/cm^2$) like $Mg_{68}Zn_{28}Ca_4$ alloy ($j_{corr} = 109 \mu A/cm^2$). Corrosion potentials (Fig. 3) of both amorphous samples are also very similar. Zheng et.al [10] performed potentiodynamic corrosion resistance tests on $Mg_{70}Zn_{25}Ca_5$ and $Mg_{66}Zn_{30}Ca_4$ amorphous alloys samples. Potentiodynamic test results from this work correspond to the Zheng's et al. [10] results. The $Mg_{66}Zn_{30}Ca_4$ alloy sample showed very similar value of the corrosion potential ($E_{corr} = -1.2$ V).

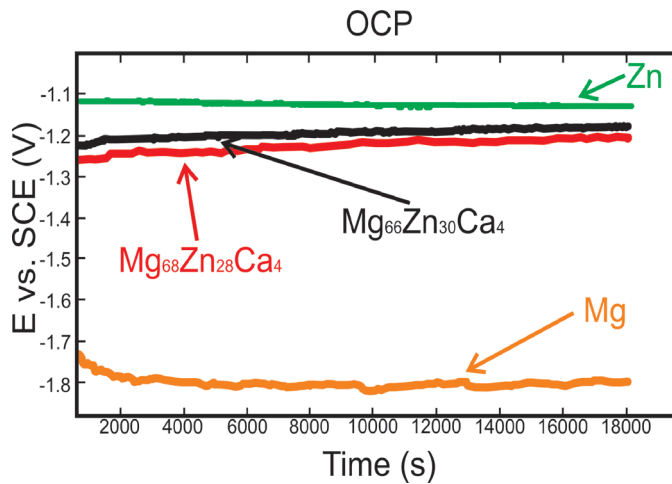


Fig. 2. Changes of open circuit potential attributed to the pure Mg, Zn, $Mg_{66}Zn_{30}Ca_4$ and $Mg_{68}Zn_{28}Ca_4$ alloys in MPF physiological fluid environment

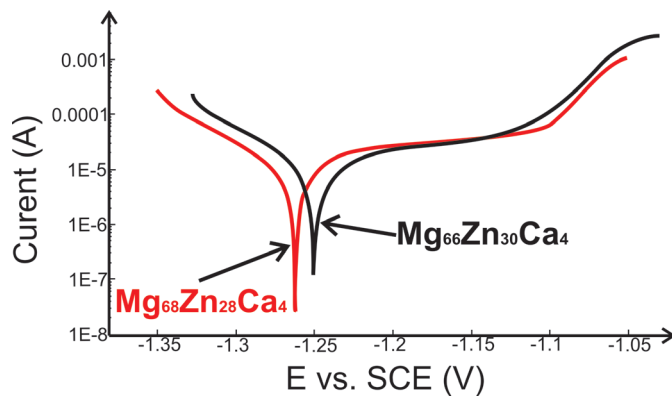


Fig. 3. Potentiodynamic curves of $Mg_{66}Zn_{30}Ca_4$ and $Mg_{68}Zn_{28}Ca_4$ alloys in MPF physiological fluid environment

Immersion tests were done to determine an amount of hydrogen evolved by $Mg_{66}Zn_{30}Ca_4$ and $Mg_{68}Zn_{28}Ca_4$ amorphous alloys after 24 hours of immersion in MPF solution (Fig.4). For $Mg_{66}Zn_{30}Ca_4$ alloy after 24 hours of immersion 0.1 ml/cm^2 of hydrogen was evolved whereas for the $Mg_{68}Zn_{28}Ca_4$ alloy it was 0.15 ml/cm^2 . Li. et al. [16] studied the amount

of hydrogen evolved from $Mg_{66}Zn_{30}Ca_4$ amorphous alloy. In the first phase, after 24 h of immersion, the evolved hydrogen amount was 0.24 ml/cm^2 . It is 2-time higher than in this study (0.1 ml/cm^2). The reason for this difference may be the fact, that research was carried out in different solution. Difference may be also related to some passivation of the surface resulting from the presence in physiological solution environment saline sodium citrate MPF [20] and sodium acetate. As it is shown in Fig. 4 (SEM images), some scratches are observable on the Mg alloys surface, due to the polishing process using the SiC paper from grinding of material. After immersion a relatively flat and uniform layer is formed on all glassy alloys, which is different from the cracked layer normally formed on crystalline magnesium alloys investigated in the simulated body fluids [22,23]. The intact layers formed on the amorphous alloys could delay the corrosion process and protect the alloys from rapid biodegradation. Surfaces of the $Mg_{66}Zn_{30}Ca_4$ and $Mg_{68}Zn_{28}Ca_4$ alloys are covered with holes of different sizes. Pitting corrosion and non-uniform corrosion are the most common phenomena during the corrosion of Mg alloys, especially when they are exposed to the solution containing chloride ions [22].

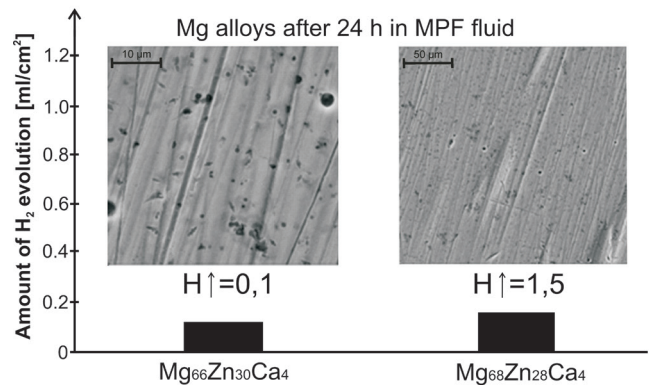


Fig. 4. Amount of evolved hydrogen and surface morphology (SEM images) after 24 hours of immersion in MPF fluid for $Mg_{66}Zn_{30}Ca_4$ and $Mg_{68}Zn_{28}Ca_4$ glassy metallic alloys

It was found, that the results of potentiodynamic tests are consistent with the results of the immersion tests (Table 2). If the corrosion potential is less negative (E_{corr} , $-1,25V$ for $Mg_{66}Zn_{30}Ca_4$, E_{corr} , $-1,263V$ for $Mg_{68}Zn_{28}Ca_4$), then less hydrogen is produced. Such relation was presented by Song et al. [21], demonstrating that hydrogen evolution rate increases as the polarisation current density or a potential becomes more positive.

To determine the amount of Mg, Zn, Ca dissolved after 24 hours of immersing the more thorough studies on MPF solution composition was done. Concentration of Mg, Zn, Ca in MPF solution before and after immersion tests was specified using inductively coupled plasma atomic emission

TABLE 1
Chemical composition of the multielectrolyte physiological fluid (MPF) used for electrochemical and immersion tests

component	NaCl	KCl	CaCl ₂ ·6H ₂ O	MgCl ₂ ·6H ₂ O	CH ₃ COONa·3H ₂ O	C ₆ H ₅ Na ₃ O ₇ ·2H ₂ O
concentration [g/dm ³]	5.750	0.380	0.394	0.200	4.620	0.900

TABLE 2

Corrosion tests results of the studied samples in MPF fluid ($E_{OC(5h)}$ – open circuit potential (V), E_{corr} – corrosion potential (V), R_p , $\Omega \cdot \text{cm}^2$ – polarization resistance, j_{corr} – corrosion current density (mA/cm^2), H_2 , amount of hydrogen evolved after 24 h (ml/cm^2), V_{corr} – corrosion rate (mm/year))

Sample	$E_{OC(5h)}$ vs. SCE [V]	E_{corr} vs. SCE [V]	R_p [$\Omega \cdot \text{cm}^2$]	j_{corr} [$\mu\text{A}/\text{cm}^2$]	H_2 [ml/cm^2]	V_{corr} [mm/year]
$\text{Mg}_{66}\text{Zn}_{30}\text{Ca}_4$ amorph	-1.180	-1.250	1.470	93	0.1	1.18
$\text{Mg}_{68}\text{Zn}_{28}\text{Ca}_4$ amorph	-1.200	-1.263	1.503	109	0.15	1.38

TABLE 3

ICP test results for the MPF fluid after immersion of the studied alloys

Concentration [mg/l]	Mg mg/l	Zn mg/l	Ca mg/l
MPF fluid before the corrosion tests	22.8	< 0.01	66.8
MPF fluid after immersion of $\text{Mg}_{66}\text{Zn}_{30}\text{Ca}_4$ alloy / 24h	26.8	0.60	68.6
MPF fluid after immersion of $\text{Mg}_{68}\text{Zn}_{28}\text{Ca}_4$ alloy / 24h	27.9	0.63	72.8

spectrometry (ICP-AES). The highest concentration of Mg, Zn and Ca in MPF fluid after 24h of immersion was observed for $\text{Mg}_{68}\text{Zn}_{28}\text{Ca}_4$ alloy. Zinc concentrations in MPF fluid after corrosion tests for both investigated alloys are very similar.

4. Conclusions

It can be concluded, that increase of Zn concentration in magnesium alloy has favorable impact on corrosion resistance within the studied samples. The amount of Mg, Zn, Ca dissolved from both Mg-based amorphous alloys after 24h of immersing in physiological fluid does not exceed the daily demand of these elements (magnesium: 300-400 mg/24h, calcium: 1000 mg/24h, zinc: 15 mg/24h [19]). Due to this fact and biocompatible chemical composition, both examined Mg-based metallic glasses can be classified as a potential biomaterial for medical implants.

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